

Statistical and Low Temperature Physics (PHYS393)

7. Cooling techniques and liquid helium

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7. Cooling techniques and liquid helium

7.1 Introduction

7.2 Liquids at low temperatures

7.3 Solids at low temperatures

7.4 Calorimetry

7.5 The helium-4 refrigerator

7.6 Exercises

Aim

To understand the basic techniques required to cool down to liquid helium temperatures.

Objectives

1. To explain how air and helium are liquefied.
2. To describe the basic properties of liquid helium.
3. To explain the behaviour of heat capacities of solids.
4. To explain how to measure heat capacity.
5. To describe the helium-4 refrigerator.

7.1 Introduction

Uses of low temperatures

The branch of physics which deals with the production of very low temperatures and their effect on matter is called cryogenics.

Liquid natural gas (LNG) is one of the main applications.



Ph. Lebrun, "An introduction to cryogenics," CERN/AT 2007-1.

The ship on the left carries $100,000 \text{ m}^3$ of LNG.
On the right is a cryogenic plant for fractional distillation of air.

Uses of low temperatures

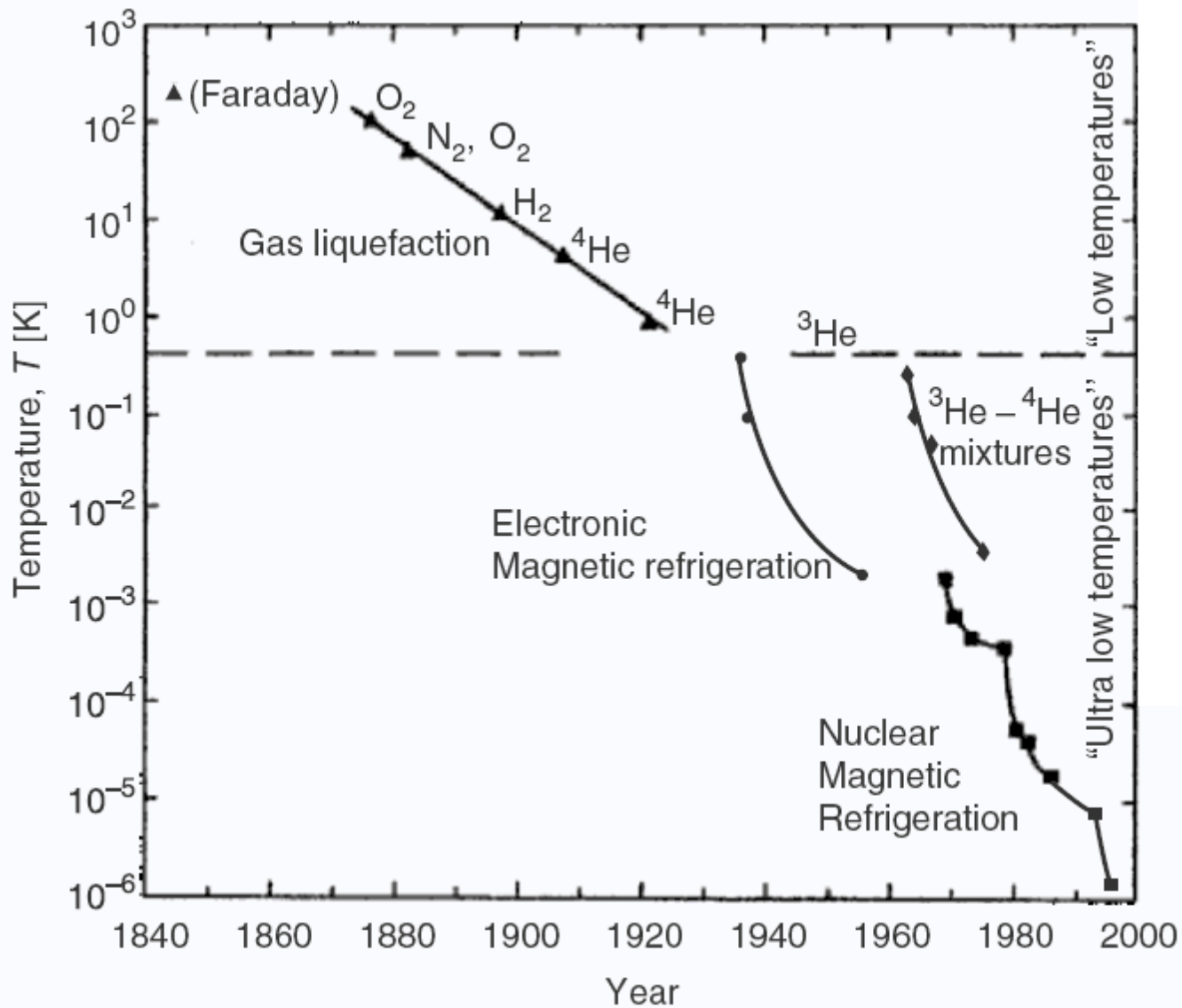
The space shuttle on the left carries 600 tonnes of liquid oxygen and 100 tonnes of liquid hydrogen.



Ph. Lebrun, "An introduction to cryogenics," CERN/AT 2007-1.

On the right is a liquid hydrogen fuel tank for a car.

The history of low temperatures



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The history of low temperatures

19th century: Air, N_2 , O_2 , H_2 were liquefied, reaching temperatures of 20 K. The practical aim was to find a way to refrigerate meat from other continents. The scientific aim was to discover whether a permanent gas exists.

1908: Helium-4 was liquefied in Leiden. This led to the discovery of superconductors and superfluid.

1922: By pumping on the vapour above a bath of Helium-4, 0.83 K was reached.

1930s: Magnetic refrigeration was invented. This would eventually reach microKelvin temperatures when it was perfected a few decades later.

1960s: The dilution refrigerator was invented, eventually reaching milliKelvin temperatures.

Refrigeration techniques

Three refrigeration methods dominate low-temperature physics today. These are given in bold in the following table.

Temperature range		Refrigeration technique	Available since	Typical T_{\min}	Record T_{\min}
I	Kelvin	Universe			2.73 K
		Helium-4 evaporation	1908	1.3 K	0.7 K
		Helium-3 evaporation	1950	0.3 K	0.23 K
II	Milli-kelvin	^3He–^4He dilution	1965	10 mK	2 mK
		Pomeranchuk cooling	1965	3 mK	2 mK
		Electronic magnetic refrigeration	1934	3 mK	1 mK
III	Micro-kelvin	Nuclear magnetic refrigeration	1956	100 μK	1.5 μK^{a}

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The 4 main challenges of low temperature

Lounasmaa (1974):

1. How to reach the low temperature?
2. How to measure it?
3. How to reduce the external heat leak so that the low temperature can be maintained for a sufficiently long time?
4. How to transfer cold from one place to another?

In these lectures, we shall mainly concern ourselves with the first one.

7.2 Liquids at low temperatures

To liquefy Air

I shall start with the liquefying of air. The same principles are used in liquefying helium.

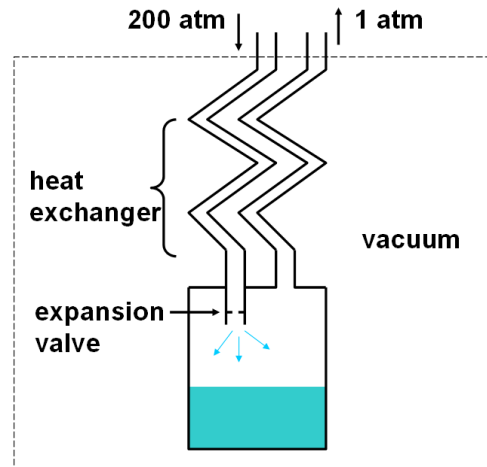
The cooling of air is achieved by expansion.

In an ideal gas, expansion against a moving piston converts internal energy to work, thus cooling it down.

In a real gas, work must also be done against the attraction between atoms or molecules. This work is much larger than the work done against the moving piston, and is the principal means of cooling. It is called the Joule-Thomson effect.

To liquefy Air

Air is first compressed to high pressure. It is then allowed to expand. This cools it down and liquefies it.



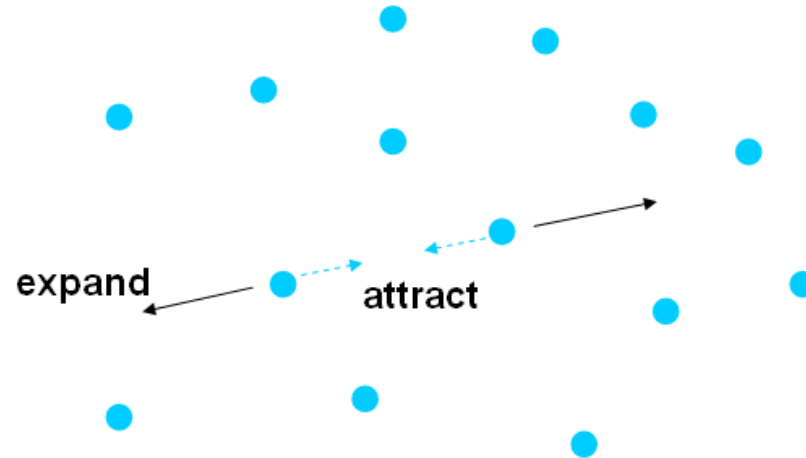
Note that the tube carrying the cold air out has to be in close contact with the tube carrying the air in.

This is an important feature called "heat exchanger." It cools down the incoming air first.

Liquid nitrogen and oxygen are then obtained from liquefied air by fractional distillation.

The Joule-Thomson (or Joule-Kelvin) effect

We know there is attraction between atoms or molecules in real gases.



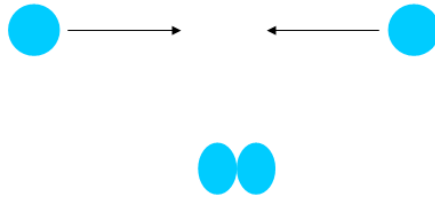
When a real gas expands, molecules do work against this attraction as they move away from one another.

They lose kinetic energy and cool down. This is true for most gases, such as oxygen and nitrogen.

There are exceptions, like hydrogen and helium.

The Joule-Thomson (or Joule-Kelvin) effect

For hydrogen or helium, the atoms or molecules could hit each other so hard, that they experience very strong repulsion when they collide.



This increases their potential energy.

When allowed to expand and move further apart, this potential energy is converted to kinetic energy.

The gas would get hotter!

However, if the starting temperature is low enough, Helium can also cool when it expands.

http://en.wikipedia.org/wiki/Joule-Thomson_effect

A note about liquid hydrogen

Liquid hydrogen is used as a fuel in rockets, and less as a refrigerant.

In fact, it can become a problem in at very low temperatures. The reason is due to the heat release when para-hydrogen is converted to ortho-hydrogen.

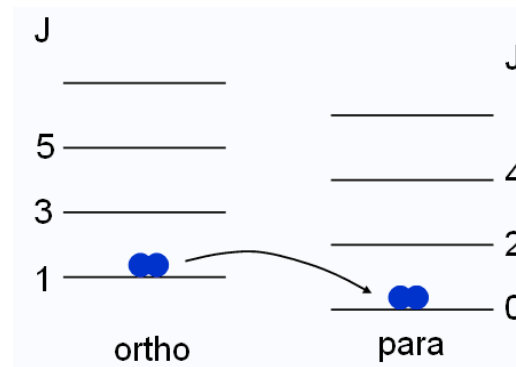
This becomes a problem because metals like copper are used in low temperature vessels, these could be manufactured by the electrolytic process.

The electrolytic process could give rise to trapped hydrogen bubbles in the metals, which would become liquefied at liquid helium temperatures.

A note about liquid hydrogen

At room temperature, 75% of hydrogen is ortho. At 20 K, only 0.2% is ortho at equilibrium.

Previously, we have learnt about the rotational energy levels of hydrogen. The lowest angular momentum for ortho-hydrogen is $J = 1$. and for para-hydrogen is $J = 0$.



As a result, the lowest energy level for ortho-hydrogen is higher than for para-hydrogen. So the conversion of ortho- to para-hydrogen releases heat energy.

A note about liquid hydrogen

The problem is, it takes a long time to achieve equilibrium, usually much longer than the cooling process.

So, while waiting to reach the final temperature, the 75% of ortho-hydrogen would convert to para-hydrogen. The heat released could cause problem for the cooling.

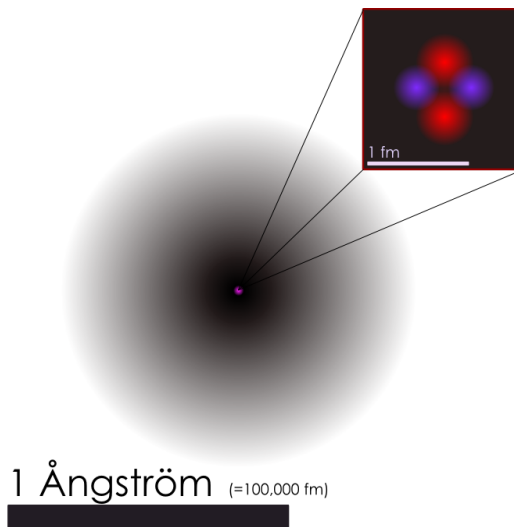
To get an idea of the amount of heat released, it is often compared with the latent heat.

The 75% of ortho-hydrogen converting to para-hydrogen releases 1.06 kJ/mol.

The latent heat of vaporisation of liquid hydrogen is 0.983 kJ/mol.

Thus, the ortho-para conversion alone is sufficient to vaporise all of the liquid.

Helium



<http://en.wikipedia.org/wiki/Helium>

In the past, helium gas was obtained from minerals. Today, it is exclusively obtained from helium-rich natural gas sources.

In both cases, it is a product of radioactive alpha decay.

There are gas sources in the USA, North Africa, Poland, the Netherlands and the former USSR.

Helium-4 (^4He) is the most common isotope of helium.

Its nucleus contains 2 protons and 2 neutrons. The total nuclear spin of helium-4 is $I=0$. So it is a boson.

Helium-3 (^3He) is a very rare isotope of helium.

The helium-3 nucleus contains 2 protons and 1 neutrons. The total nuclear spin of helium-3 is $I=1/2$. So it is a fermion.

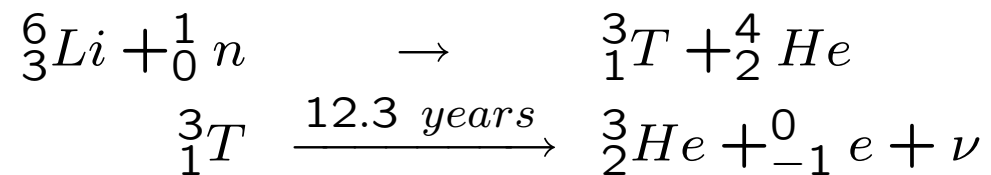
Helium-4 obeys the Bose-Einstein statistics.

Helium-3 obeys the Fermi-Dirac statistics.

Helium-3

Helium-3 is only a fraction of 10^{-7} of natural helium gas.

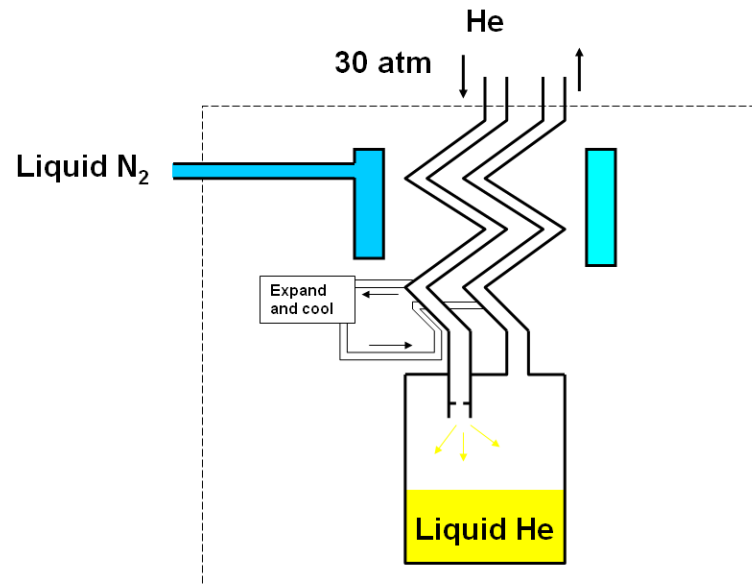
Helium-3 is very expensive to separate from the natural sources. Instead, it is obtained as a byproduct of tritium manufacture in a nuclear reactor:



It is still expensive. In 2007, it costs about 200 euros per litre of the helium-3 gas, at standard temperature and pressure.

A helium liquefier

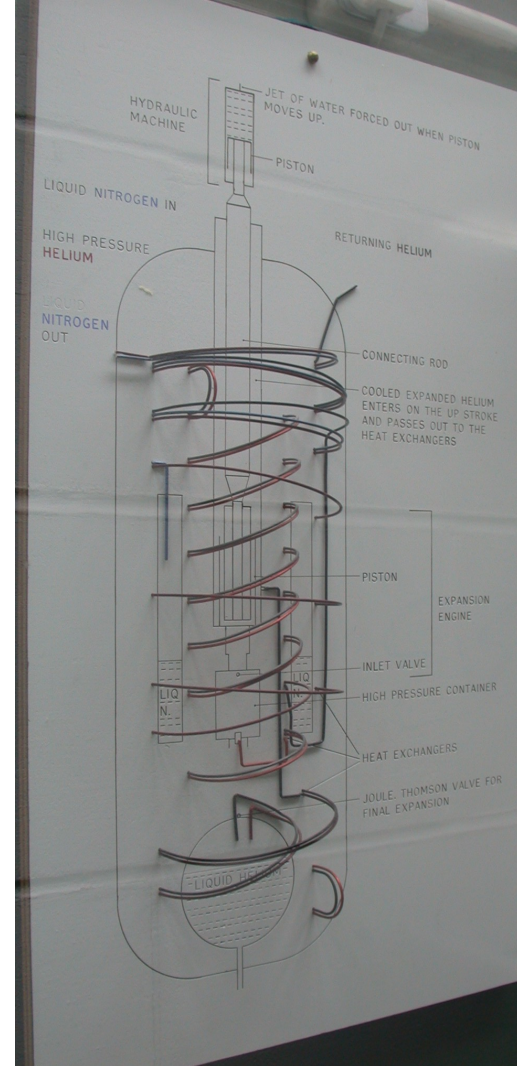
First, the helium gas is surrounded by liquid N_2 to "pre-cool" it.



Then, 90% of it is expanded into another box for further cooling, and brought back in contact with the heat exchanger.

The rest expands into the bottom box. This is cold enough for a small fraction to become liquid helium (4.2 K).

Kapitza's helium liquefier



<http://www-outreach.phy.cam.ac.uk/camphy/museum/area7/cabinet1.htm>

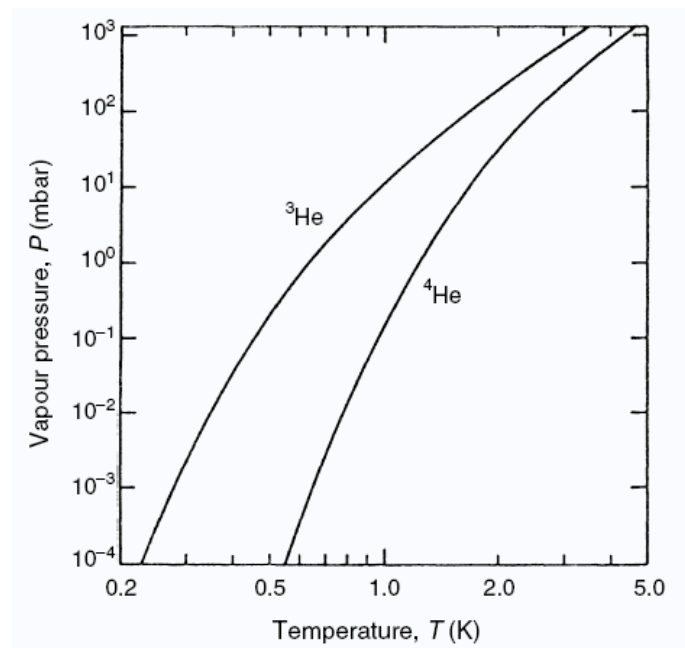
Liquid helium vapour pressure

The boiling point of helium-4 is 4.21 K.

The boiling point of helium-3 is 3.19 K.

Helium evaporation is an important cooling technique. The lowest temperature it can reach is limited by the vapour pressure, which decreases exponentially with falling temperature:

$$P_{\text{vap}} \propto \exp(-1/T).$$



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Liquid helium specific and latent heat

At low temperatures, the specific heat of liquid helium is very large compared with other materials.

At 1.5 K, the specific heat of 1 g of helium-4 is about 1 J/K.
At 1.5 K, the specific heat of 1 g of copper is about 10^{-5} J/K.

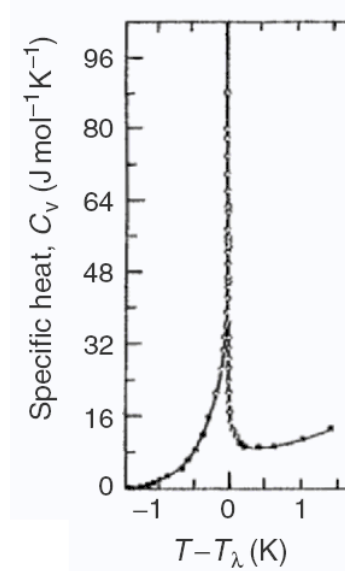
This is important. Imagine a bath of liquid helium in a copper container. Any change in temperature would be entirely due to the helium. Heat gain by the copper would be negligible.

This property means that the temperature of the whole experimental setup would rapidly follow any temperature change of the liquid helium bath.

The latent heat of vaporisation of helium is also large compared to the specific heat of other materials. This makes liquid helium effective for cooling other materials by evaporation.

Superfluid transition

There is a very sudden increase in the specific heat of helium-4 near 2.2 K. This is due to a phase transition. Below 2.2 K, helium-4 changes to a superfluid with zero viscosity.



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Because of the shape of the graph, this temperature is called the lambda (λ) point.

Helium-3 liquid can also change to a superfluid, but at the much lower temperature of 2.5 mK.

7.3 Solids at low temperatures

We shall focus on the specific heat of the various types of solids that we have seen the Part 1 of these lectures on Statistical Mechanics. For cooling techniques, the other important property is the thermal conductivity.

The following types of solid shows distinctive behaviours in specific heat at low temperatures:

- insulators
- metals
- superconductivity metals
- magnetic materials

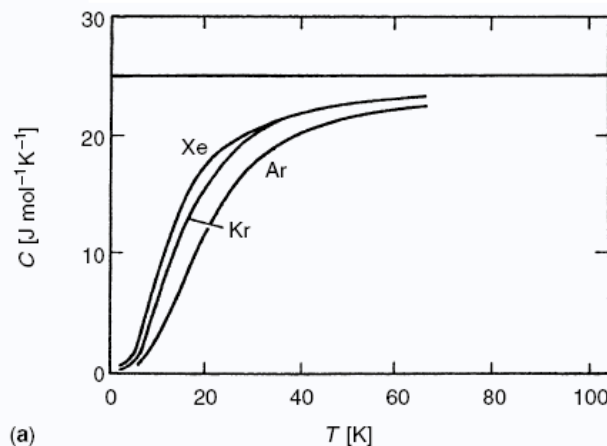
For non-magnetic, crystalline insulators, the most important and often the only possible excitations are vibration of atoms, or phonons.

We have previously learnt that at high temperatures, the atoms may be approximated by Einstein's model of independent, simple harmonic oscillators.

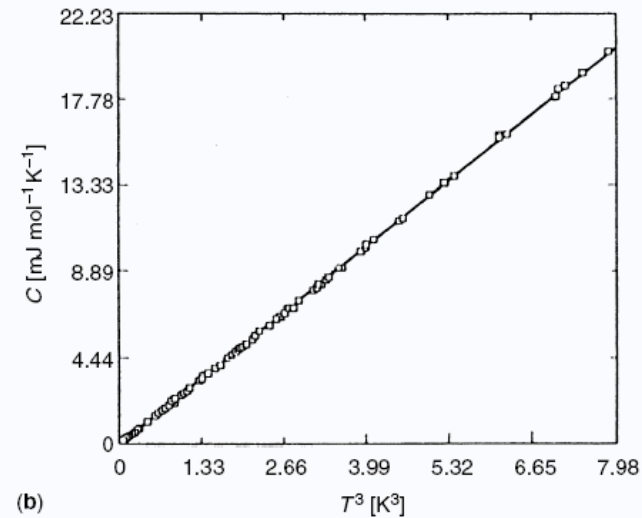
At low temperatures, however, we need Debye's phonon model to describe the coordinated lattice vibration (phonons).

Insulators

The overall behaviour of the heat capacity due to phonons is shown in the left figure. In the lectures on phonons, we have learnt that it reaches a constant at high temperature, and goes to zero at low temperature.



Specific heat of solid Ar, Kr and Xe.



Specific heat solid of Ar as a function of T^3

C. Kittel: Introduction to Solid State Physics, 8th edn. (Wiley-VCH, Weinheim 2004)
L. Finegold, N.E. Phillips: Phys. Rev. 177, 1383 (1969)

We have also seen that at low temperatures, the heat capacity is proportional to T^3 . Plotting C against T^3 would give a straight line, as shown on the right.

For T much smaller than the Debye temperature θ_D , the heat capacity is

$$C = \frac{2V\pi^2 k_B^4 T^3}{5\hbar^3 v^3}.$$

We have also seen that the Debye temperature is related to the Debye frequency by

$$k_B \theta_D = \hbar \omega_D$$

and the Debye frequency is given by

$$\omega_D = \left(\frac{6N\pi^2 v^3}{V} \right)^{1/3}.$$

Substituting into the above formula for the heat capacity, we would get

$$C = \frac{12}{5} \pi^4 N k_B \left(\frac{T}{\theta_D} \right)^3.$$

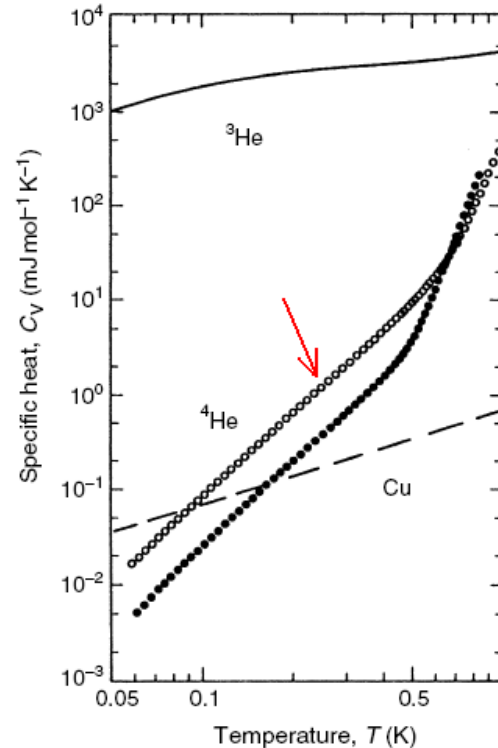
The Debye temperature is a useful reference for low temperature behaviour. Below this temperature, the phonons begin to "freeze out," meaning that not all the frequency modes would get excited.

Through the sound velocity v in the formula for ω_D above, the Debye temperature is also directly related to the bond strength and mass of the atoms. For example, for diamond it is 2000 K, and for lead it is 95 K.

Liquid helium is unusual in that it is a liquid below its Debye temperature. One possible explanation is that the atoms in the helium liquid tends to have only small oscillations.

Insulators

This is a log-log plot of the measured heat capacity against temperature. The result for liquid helium-4 at vapour pressure is given by the open circles.



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The gradient is 3, which shows that it is proportional to T^3 .
The Debye temperature estimated from this figure is 29.0 K.

In addition to phonons, a metal also has conduction electrons. Because of the large mass difference of the nuclei and electrons, the specific heat due to lattice vibration (phonons) and to conduction electrons can be treated independently and just added.

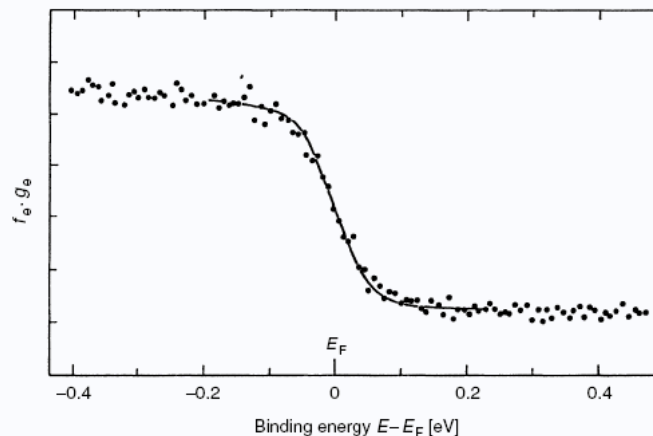
This is because to a very good approximation their motions are independent, and the Schrödinger equation for the whole crystal can be separated into an electronic part and a lattice part. (This is called the Born-Oppenheimer approximation.)

Metal

The Pauli principle means that the electrons stack up in energy levels until the Fermi energy, typically about 1 eV.

At room temperature, $k_B T$ is about 1/40 eV. So it is difficult to excite any of the electrons.

The properties of metals at low temperatures are determined exclusively by electrons in energy states very close to the Fermi level.

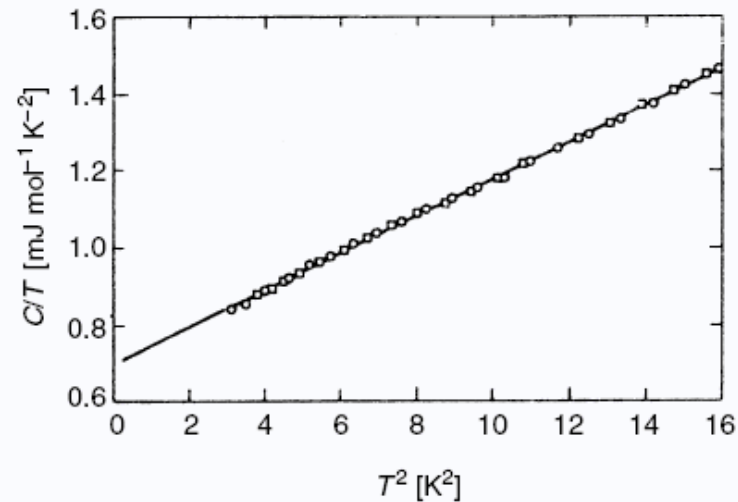


Occupied electronic states of Ag at 300 K near the Fermi energy E_F obtained from photoelectron spectroscopy. The full line is the Fermi distribution function (3.11) [3.13]

F.L. Batty, A. Goldmann, L. Kasper, S. Hüfner: Z. Phys. B 27, 209 (1977)

Metal

We have seen previously that excitations near the Fermi energy leads to the result that the specific heat is proportional to T .



Specific heat C of copper divided by the temperature T as a function of T^2

H. Ibach, H. Lüth: Solid-State Physics, An Introduction to Theory and Experiment, 2nd edn. (Springer, Berlin Heidelberg New York 1995)

This has been verified by measurement, and helps to validate the theories of quantum mechanics, the free electron model, and the Fermi-Dirac statistics.

Superconducting metals

Many metals enter into a superconducting state below a certain critical temperature. In this state, the electrical resistance drops to zero.

The reason for this is explained by Bardeen, Cooper and Schrieffer in 1957. It involves the pairing of electrons to form bosons, known as Cooper pairs, under the influence of lattice vibrations.

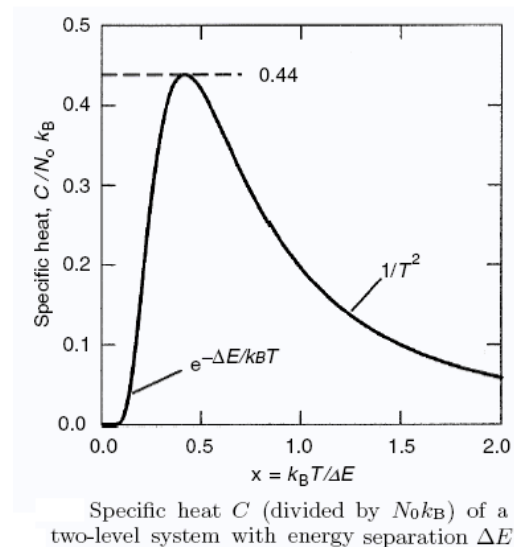
When a magnetic field above a certain critical strength is applied, it would break up the Cooper pairs, and the metal would return to the normal state.

http://physuna.phs.uc.edu/suranyi/Modern_physics/Lecture_Notes/modern_physics12.html

This effect is used in a heat switch to control the flow of heat in a metal.

Magnetic specific heats

We have previously seen that the magnetic spin states in a paramagnet contributes to the heat capacity in the form a Schottky anomaly.



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This peak in the heat capacity typically occurs at very low temperatures. On the higher temperature side, the peak falls off as $1/T^2$.

Recall that we have derived, for the spin-1/2 case, the expression for the heat capacity in the lectures on paramagnetic salts. On the higher temperature side of the Schottky anomaly, it is given by

$$C \rightarrow Nk_B \left(\frac{\mu_B B}{k_B T} \right)^2$$

which is proportional to $1/T^2$. This may also be written in the form:

$$C_m \rightarrow N_A k_B \left(\frac{\Delta E}{2k_B T} \right)^2$$

where ΔE is the difference between the magnetic energy level and N_A is the Avogadro constant. In this form, it refers to the heat capacity for one mole, or the specific heat. Note that this formula is only valid for the spin-1/2 case.

In paramagnetic salts, the magnetic energy comes from the magnetic dipole of the electrons. In a spin-1/2 salt, the difference between the magnetic energy level is

$$\Delta E = 2\mu_B B.$$

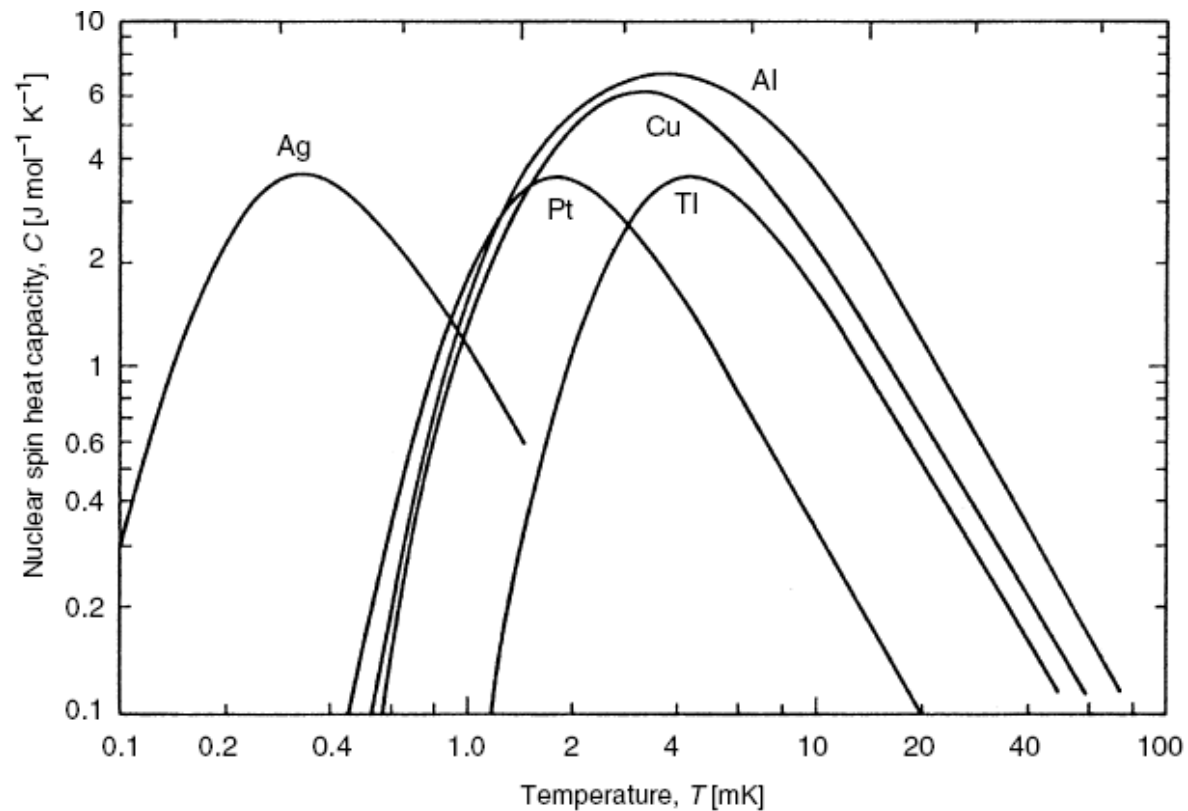
For metals, we are more interested in the magnetic dipole of the nuclei. This is because the conduction electrons can become aligned at low temperatures, so that they would not contribute to the heat capacity. For nuclear magnetic moment, the difference between the magnetic energy level is

$$\Delta E = 2\mu_n B,$$

where μ_n is the nuclear magneton. This is more than 1000 times smaller than the Bohr magneton μ_B that is used for electrons. This means that the peak of the heat capacity would occur at a much lower temperature.

Magnetic specific heats

This figure shows the nuclear heat capacities for various metals. The magnetic field applied is 9 T.



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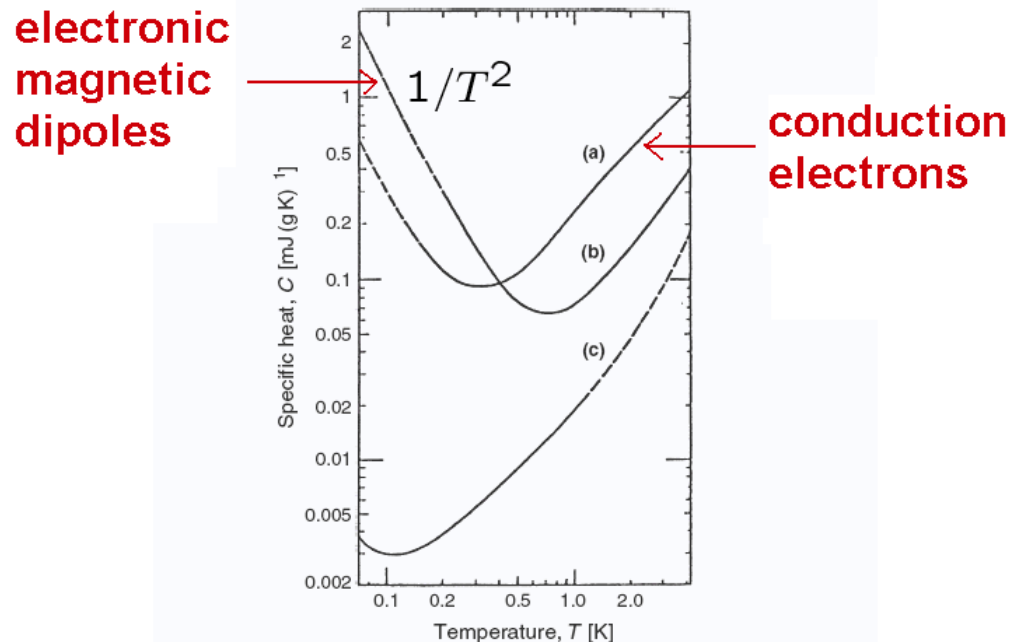
We have seen that in a metal, the electrons and phonons contribute to the specific heat. At low temperatures, the electron contribution is proportional to T , and the phonon contribution to T^3 .

This means that the phonon contribution falls off more rapidly than the electron contribution when temperature decreases. So at very low temperatures, the only contribution would come from the electrons, and this would fall linearly with T .

However, at even lower temperature, the heat capacity would rise instead. This happens when $k_B T$ become comparable with the difference in nuclear magnetic energy levels.

Magnetic specific heats

In the presence of magnetic materials, the Schottky anomaly would contribute $1/T^2$, which increases at temperature falls.



Specific heats of (a) Constantan (57% Cu, 43% Ni),
(b) Manganin (87% Cu, 13% Mn) and (c) a 9% W, 91% Pt alloy

J.C. Ho, N.E. Phillips: Rev. Sci. Instrum. 36, 1382 (1965)

This could be a problem. For example, platinum is the "workhorse" of temperature measurement at mK and μK temperatures. Iron impurities in a few parts per million can increase the specific heat of platinum in a small magnetic field (about 0.01 T) by one order of magnitude.

7.4 Calorimetry

How to measure heat capacity:

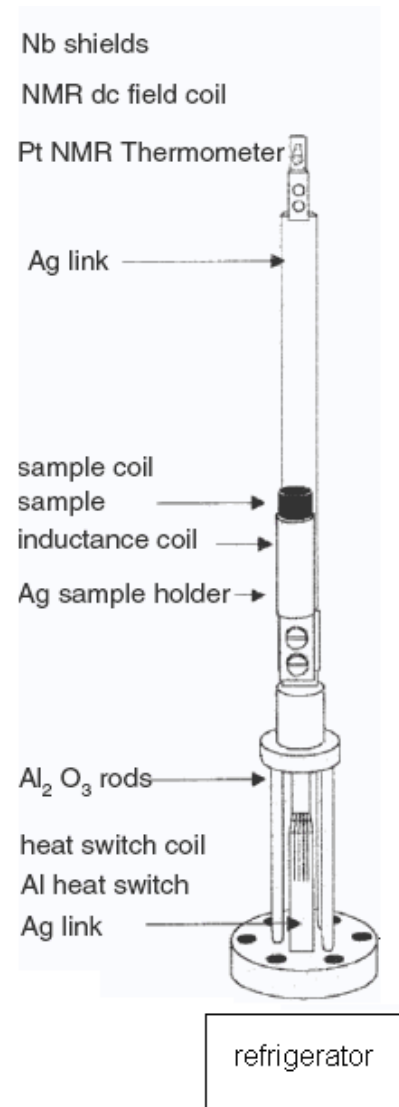
1. Refrigerate the material of mass m to the starting temperature of T_i .
2. Isolate it thermally from its environment (e.g. by opening a heat switch).
3. Supply some heat P to reach the final temperature T_f .
4. The result is

$$\frac{C}{m} = \frac{P}{T_f - T_i}$$

at the intermediate temperature

$$T = \frac{T_f + T_i}{2}.$$

A low temperature calorimeter



T. Herrmannsdörfer, F. Pobell: J. Low Temp. Phys. 100, 253 (1995)

A low temperature calorimeter

At low temperatures, there are many problems:

1. Power needed to read the thermometer could overheat it.
2. Radiation causes heat loss or inflow.
3. Opening of heat switch produces heat.
4. Gas vaporising from a surface removes heat.
5. It takes a long time to reach thermal equilibrium.

Precautions can be taken to minimise the errors due to these effects, but it is difficult.

Heat capacity data rarely have an accuracy better than 1%.

Heat switch

The heat switch is a way to isolate a sample once it has cooled down to the required temperature.

There are a few possible ways at higher temperatures. One way is to use a helium gas to mediate the cooling, and then remove it by pumping to isolate the sample. Another is to use a good conductor for cooling, and then physically disconnect it.

At very low temperatures, these are not suitable. The helium exchange gas would have liquefied. The mechanical breaking of contact would generate too much heat.

For temperatures below 1 K, a superconductor has to be used.

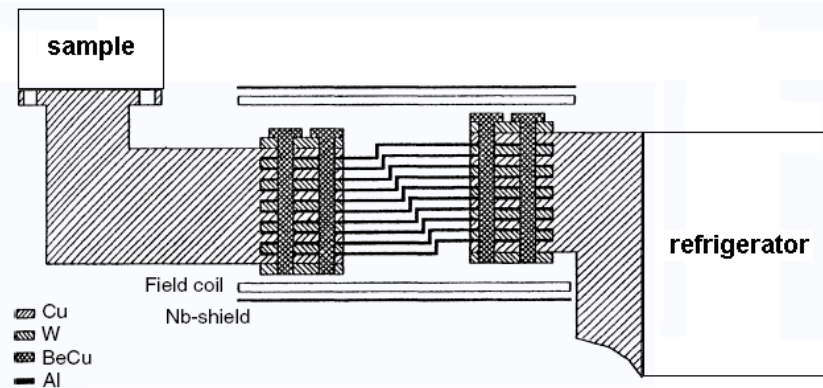
The thermal conductivity of a metal in the superconducting state can become very small.

This is because the most of the free electrons have been bound up into Cooper pairs. The thermal conductivity can be much smaller than that of the same metal in the normal conducting state.

Some metals can easily be switched from the superconducting to the normal state by applying a magnetic field. This property can be used to build a "superconducting heat switch."

Superconducting heat switch

In this figure, the aluminium in the middle becomes superconducting at low temperatures. The sample is on one side, and the refrigerator is on the other side.

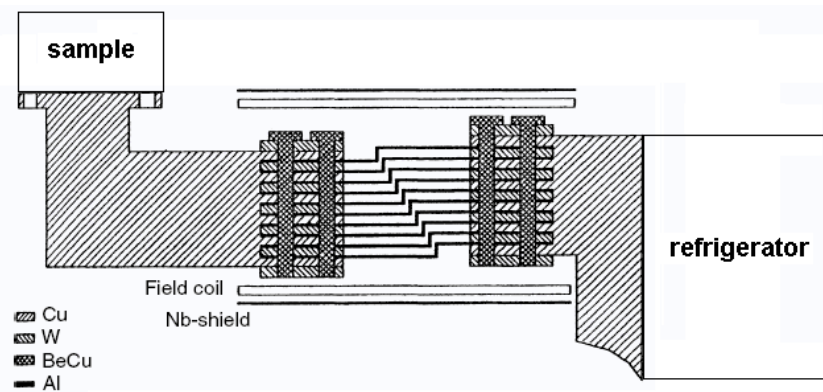


T. Okamoto, H. Fukuyama, H. Ishimoto, S. Ogawa: Rev. Sci. Instrum. 61, 1332 (1990)

This is surrounded by a solenoid. When an electric current is passed into the solenoid, the magnetic field penetrates into the aluminium and changes it to the normal conducting state.

Superconducting heat switch

In order to cool down the sample, the aluminium has to be in the normal conducting state to conduct heat from the sample to the refrigerator.



T. Okamoto, H. Fukuyama, H. Ishimoto, S. Ogawa: Rev. Sci. Instrum. 61, 1332 (1990)

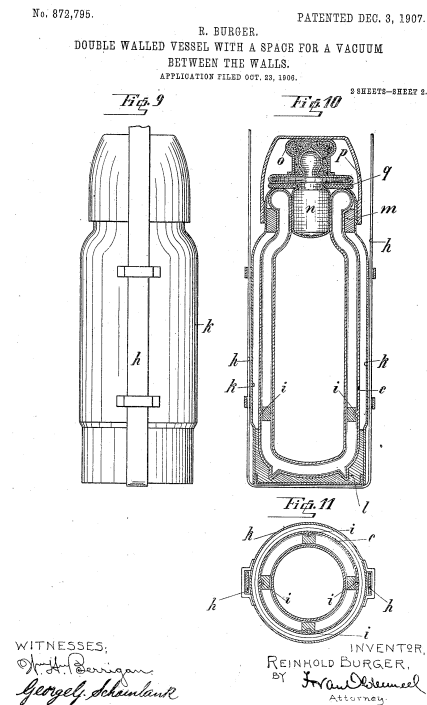
Once the sample has cooled down, the magnetic field is switched off. The aluminium changes to the superconducting state. The thermal conductivity falls, and the sample gets isolated from the refrigerator.

7.5 The helium-4 refrigerator

What do we use for storing liquid gases?

We have used it to store our hot coffee.

"The vacuum flask was invented by Scottish physicist and chemist Sir James Dewar in 1892 and is sometimes referred to as a Dewar flask after its inventor."

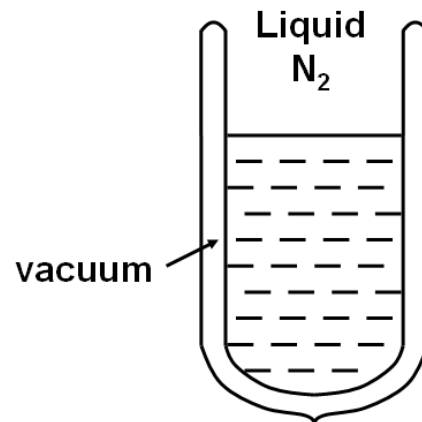


http://en.wikipedia.org/wiki/James_Dewar
<http://en.wikipedia.org/wiki/Thermos>

It is also called the vacuum flask or thermos flask.

The dewar.

A dewar,
or a styrofoam container that is quite common in the lab,

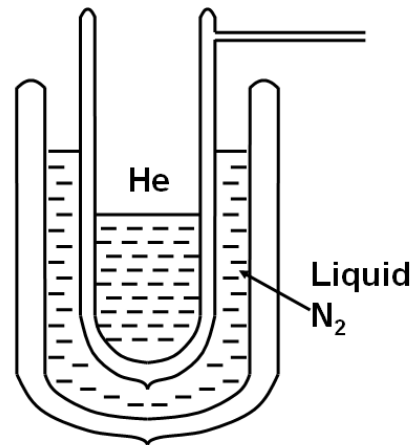


is quite sufficient for liquid nitrogen (77 K).

Storing liquid helium is more tricky.

It is a lot colder (4.2 K), and it could diffuse through glass!

A dewar of liquid helium is usually placed inside a dewar of liquid nitrogen.



The problem with the diffusion of helium is that it degrades the vacuum in the dewar. Either it must be evacuated continually, or it could be made of metal.

The helium-4 cryostat

In order to contain liquid helium, a special vessel is required.

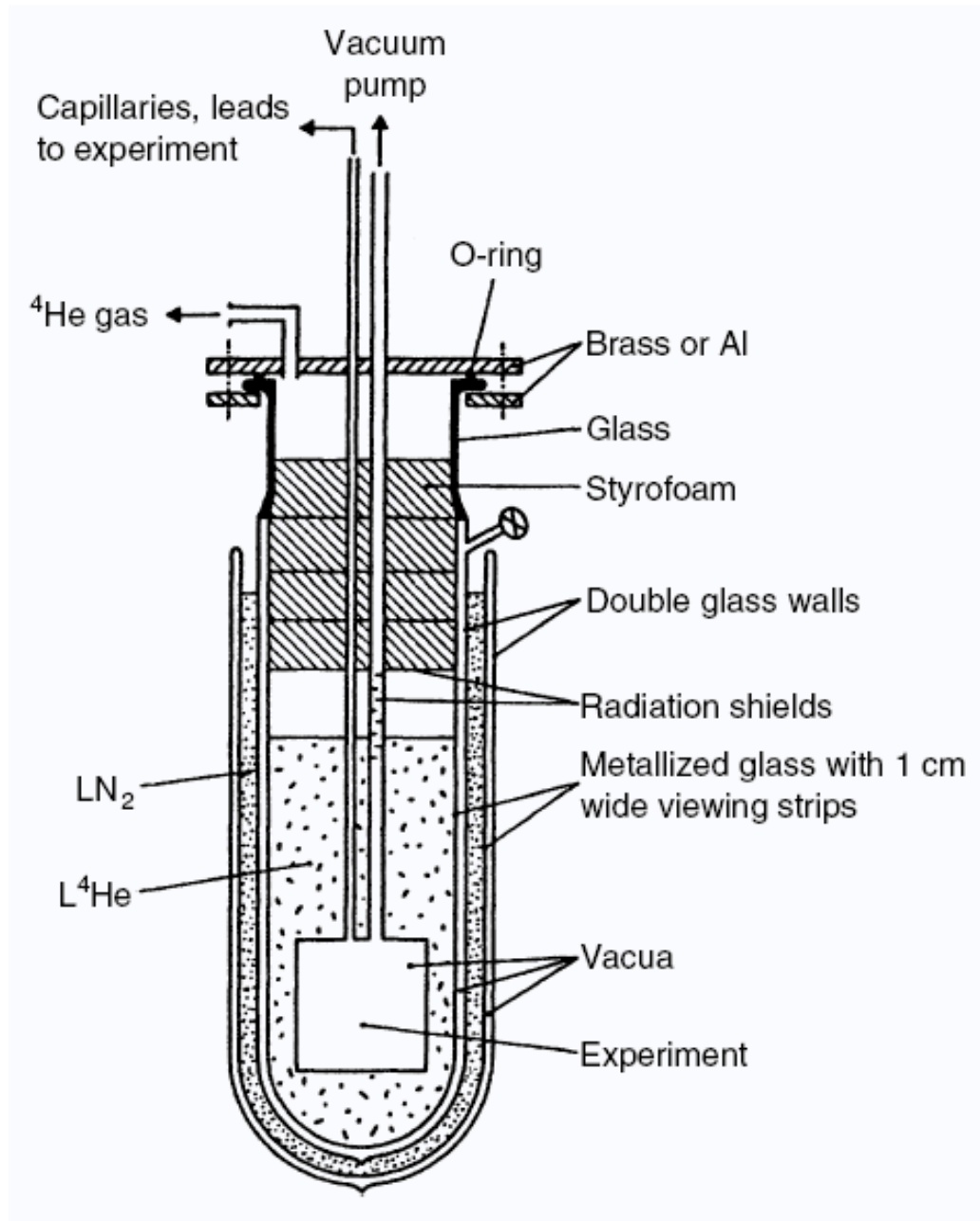
This vessel is called a cryostat. It must be able to isolate the liquid helium from the room temperature.

A helium cryostat is essentially a large vacuum flask, often with an additional layer of liquid nitrogen surrounding the helium liquid.

Low temperature experiments would be carried out in a small chamber in the cryostat next to the helium bath. This could be measuring heat capacity, or observing superconducting or superfluid behaviours.

In order to control the experiments, it is also necessary to have electrical wires running into the cryostat.

The helium-4 cryostat

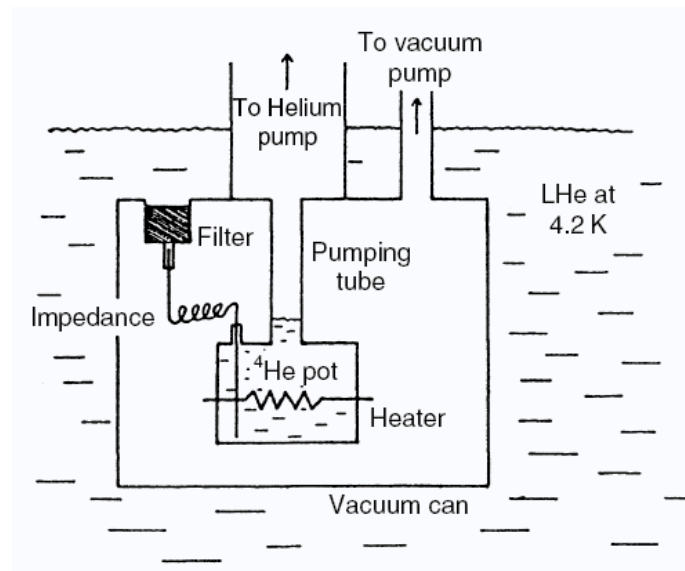


Pobell (2007)

The helium-4 evaporation refrigerator

A liquid helium-4 bath on its own would have a temperature of about 4.2 K, the boiling temperature of helium-4.

It is possible to reduce this temperature by increasing the evaporation rate. This is done by pumping away the helium vapour.



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Using this method, it is possible to reach 1.3 K. It is difficult to go below this because the vapour pressure decreases exponentially with falling temperature.

The helium-3 evaporation refrigerator

It should be mentioned that we can reach further down to 0.3 K if we use helium-3 instead of helium-4.

The main reason is that helium-3 has a higher vapour pressure, and therefore a higher vaporisation rate. This is due to the lower mass of the helium-3 atom.

The helium-3 evaporation refrigerator is similar in design to the helium-4 evaporation refrigerator.

The disadvantage of using helium-3 is the high cost.

7.6 Exercises

Exercise 1

Show that at room temperature, normal H_2 contains 75% ortho-hydrogen and 25% para-hydrogen.

[You are given that the moment of inertia of the H_2 rotator is $I = 4.59 \times 10^{-48} \text{ kg m}^2$.]

Lets start by getting some idea of the energy and population at each energy level. The energy is given by

$$\varepsilon_J = \frac{\hbar^2}{2I} J(J+1)$$

Substituting the values of \hbar and I , we can calculate the following at room temperature (298 K):

J	$\exp(-\varepsilon_J/k_B T)$	ε_J/k_B (K)
0	1	0
1	0.5576	174.1
2	0.1734	522.2
3	0.0301	1044

The second column tells us the relative population at each level, and the third column allows us to compare each level with room temperature. For $J > 3$, the Boltzmann factors would be quite small, so we shall use only the terms up to $J = 3$.

We can calculate the proportion of ortho and para-hydrogen at room temperature.

The mean number of particles at each energy level for para-hydrogen is given by

$$n_J = N \frac{(2J + 1) \exp(-\varepsilon_J/k_B T)}{Z}$$

The number of para-hydrogen molecules is

$$N_{\text{para}} = N \frac{\sum_{J \text{ even}} (2J + 1) \exp(-\varepsilon_J/k_B T)}{Z}.$$

The mean number of particles at each energy level for ortho-hydrogen is given by

$$n_J = N \frac{3(2J + 1) \exp(-\varepsilon_J/k_B T)}{Z}$$

where the factor of 3 comes from the spin degeneracy. The number of ortho-hydrogen molecules is

$$N_{\text{ortho}} = N \frac{\sum_{J \text{ odd}} 3(2J + 1) \exp(-\varepsilon_J/k_B T)}{Z}.$$

The proportion ortho and para-hydrogen is then

$$\frac{N_{\text{ortho}}}{N_{\text{para}}} = \frac{\sum_{J \text{ odd}} 3(2J + 1) \exp(-\varepsilon_J/k_B T)}{\sum_{J \text{ even}} (2J + 1) \exp(-\varepsilon_J/k_B T)}.$$

Substituting the results from the above table, we get 2.98, or about 3. This means that at room temperature, there is 75% ortho- and 25% para- hydrogen.

Exercise 2

At room temperature, normal H_2 contains 75% ortho-hydrogen and 25% para-hydrogen. When cooled down to 20 K (the boiling point), it would take some time before most of the ortho-hydrogen is converted to para-hydrogen.

Calculate the heat energy released when one mole of normal H_2 at 20 K is converted to one mole of para- H_2 .

Given that the latent heat is 0.94 kJ/mol, what would then happen to the liquid hydrogen?

[You are given that the moment of inertia of the H_2 rotator is $I = 4.59 \times 10^{-48} \text{ kg m}^2$.]

Lets start by getting some idea of the energy and population at each energy level. The energy is given by

$$\varepsilon_J = \frac{\hbar^2}{2I} J(J + 1)$$

Substituting the values of \hbar and I , we can calculate the following at 20 K:

J	$\exp(-\varepsilon_J/k_B T)$
0	1
1	0.0002
2	5×10^{-12}
3	2×10^{-23}

From the rapid decrease in the Boltzmann factor, we see that only the lowest state would be occupied. So only the lowest state for para- and ortho-hydrogen need to be considered.

For normal hydrogen at 20 K, 75% would be at the ground state of ortho-hydrogen, and 25% would be at the ground state of para-hydrogen.

This means that 75% would have $J = 1$, and 25% would have $J = 0$. When the 75% converts to para-hydrogen, the difference in energy would be given out as heat.

This energy difference for one molecule would be given by

$$\varepsilon_J = \frac{\hbar^2}{2I} J(J+1)$$

for $J = 1$. In one mole of normal hydrogen, the number of ortho-hydrogen molecules would be $0.75N_A$. When these are converted to para-hydrogen, the heat given out would be

$$Q = 0.75N_A\varepsilon_1 = 0.75N_A\frac{\hbar^2}{I}$$

Substituting the moment of inertia I and values for the constants, we find 1.08 kJ/mol.

So this is the heat energy released when one mole of normal H_2 at 20 K is converted to one mole of para- H_2 .

Since the latent heat of 0.94 kJ/mol is smaller than this heat release, all of the liquid hydrogen would be vaporised by this ortho to para conversion alone.

Exercise 3

Calculate the Debye temperature corresponding to the heat capacity C_V of liquid helium-4 for temperature $T < 0.5$ K. The following data is obtained from a graph the measured data in which $\log C_V$ is plotted against $\log T$.

log-log plot of the measured data:

$$T = 0.5 \text{ K}, C_V = 0.01 \text{ J/(mol.K)}$$
$$\text{gradient} = 3$$

The units of the heat capacity is given as J/(mol.K). This refers for 1 mole of the liquid.

So the heat capacity formula for insulators at low temperature can be written as

$$C = \frac{12}{5} \pi^4 N_A k_B \left(\frac{T}{\theta_D} \right)^3 .$$

where the number of particles N is replaced by Avogadro's constant N_A .

The power of 3 agrees with the gradient of 3 from the log-log plot.

Substituting the given data:

$$T = 0.5 \text{ K}, C_V = 0.01 \text{ J/(mol.K)}$$

into the above formula, we can then solve for θ_D . The answer is 29.0 K.

Exercise 4

At which temperature do the lattice and conduction electron contributions to the heat capacity of copper become equal?

The following data are obtained from a straight line graph of C/T plotted against T^2 , where C is the measured heat capacity and T is the temperature:

$$\text{gradient} = 0.0469 \text{ mJ mol}^{-1} \text{ K}^{-4}$$

$$\text{vertical intercept} = 0.7 \text{ mJ mol}^{-1} \text{ K}^{-2}$$

Since the graph of C/T against T^2 is a straight line, they are related by the straight line equation:

$$\frac{C}{T} = \gamma + AT^2.$$

Multiplying by T , we get

$$C = \gamma T + AT^3.$$

The electronic contribution is linear in T , so it would be given by the first term:

$$C_e = \gamma T.$$

The lattice (phonon) contribution is proportional to T^3 , so it would be the second term:

$$C_{ph} = AT^3.$$

When they become equal, we can solve these 2 equations for T . This gives:

$$T = \sqrt{\frac{\gamma}{A}}.$$

We can find γ and A from the graph. Returning to the straight line equation

$$\frac{C}{T} = \gamma + AT^2.$$

we can see that γ would be the vertical intercept, and A would be the gradient. These 2 values are given. Substituting, we find:

$$T = \sqrt{\frac{0.7}{0.0469}} = 3.86\text{K}.$$

Remark: Since the phonon contribution varies as T^3 , it would fall off much faster than the electronic contribution as temperature decreases. So below 3.86 K, the electrons would be the main contributor, and the heat capacity would be approximately linear.

Exercise 5

At which temperature is the nuclear magnetic contribution in a field of 100 mT equal to the conduction electron contribution to the heat capacity of silver?

[You are given that the nuclear spin of silver is $1/2$.
The nuclear magneton is $\mu_n = 5.051 \times 10^{-27} \text{ J T}^{-1}$.
For the heat capacity of silver, $\gamma = 0.640 \text{ mJ mol}^{-1} \text{ K}^{-2}$.]

On the higher temperature side of peak of the magnetic contribution, the magnetic heat capacity per mole is given by

$$C_m \rightarrow N_A k_B \left(\frac{\Delta E}{2k_B T} \right)^2$$

where

$$\Delta E = 2\mu_n B.$$

At low temperature, the electronic heat capacity per mole of copper is

$$C_e = \gamma T.$$

When the electronic and nuclear magnetic contributions become equal,

$$C_e = C_m.$$

Solving for T , we get

$$T^3 = \frac{N_A k_B}{\gamma} \left(\frac{\Delta E}{2k_B} \right)^2.$$

Substituting the values given and the constants, we find 25.9 mK.

Remark: So below this temperature, we would find that the heat capacity stops falling and rise instead. It would then be dominated by the magnetic contribution.